

**Design Patent**

DE 295 12 302 U 1

International class: A 61K 7/13

C 08 L 5/00

//C08B 37/00.A 61K

7/08

File: 295 12 302.8

Date of submission: 31 July 1995

Date of entry: 28 November 1996

Publication in Patent Gazette: 16 January 1997

Owner: Kao Corp., Tokyo, Japan

Representative: Hoffman, Eitle &amp; Partner Patent Attorneys, DE-81925 Munich

**Means of toning human hair**

The present invention concerns a means of dyeing or toning human hair with improved color intensity, at the same time exhibiting improved stability.

It is generally known that hair dyeing means may be divided into two categories: one, the permanent hair dyes that contain basic hair dyeing products that develop the desired color on the hair together with oxidizing agents, depending upon formulation and, two, the semi-permanent hair dyeing means that contain direct-acting dyes that do not require any additional means of oxidation for the development of their color properties. Accordingly, the colors are also less durable than those achievable with permanent dyes.

These dyeing preparations based upon direct-acting dyes are generally applied either as toning shampoos, as lotions or toning fixes and occasionally also as aerosol foam.

These preparations, insofar as solutions or lotions are concerned, frequently contain stabilizers with thickening action, particularly cellulose derivatives such as hydroxethyl cellulose, for example,

However, the stability and color intensity achievable from these preparations is not satisfactory.

There exists, therefore, a requirement for hair dyeing products based upon direct-acting dyes that are stable and that exhibit improved coloring properties compared to the usual formulations.

The present invention provides a means of dyeing and toning human hair that contains at least one direct-acting dye as well as 0.1 to 7.5, preferably 0.25 to 5, particularly 0.5 to 2.5% by weight, based on the total mixture, of at least one hydroxy-C<sub>2</sub>-C<sub>4</sub>-alkyl guar gum and/or a quaternary product of this.

The color intensity, that is, the ability to absorb dye, is substantially improved, compared to current products, by the addition of the hydroxyalkyl guar derivative; the product also exhibits excellent stability.

The pH value of the means according to the invention lies in the range of 2 to 10, preferably between 4 and 9, particularly between approximately 6 and approximately 8.

Hydroxypropyl guar is the preferred hydroxy-C<sub>2</sub>-C<sub>4</sub>-alkyl guar gum derivative that is, as previously mentioned, contained in the hair coloring and toning means according to the invention in a quantity of 0.1 to 7.5, preferably 0.25 to 5, particularly 0.5 to 2.5% by weight, that is, the propylene glycol ester of guar, as well as the quaternary products of this, in particular, hydroxypropyl guar hydroxypropyl trimonium chloride. Other appropriate hydroxalkyl guar derivatives are hydroxethyl guar, hydroxybutyl guar and their quaternary products, for example.

Suitable commercial products are on the market under the trade names "Jaguar HP®," "Jaguar C-17®," "Jaguar C-162®" and "Galactosol®."

In principle, all of the permitted dyes can be used for this purpose as direct-acting hair dyes. This is particularly referred to in the German Statute Concerning Cosmetic Preparations (Cosmetics Statute) in its current version, Supplement 3.

However, the cationic (basic) dyes are particularly preferred since their stability and dye uptake properties are especially enhanced by the addition of the guar gum derivative according to the invention.

Particularly suitable basic (cationic) dyes are:

Basic Blue 6	C. I. No. 51,175
Basic Blue 7	C. I. No. 42,595
Basic Blue 9	C. I. No. 52,015
Basic Blue 26	C. I. No. 44,045
Basic Blue 41	C. I. No. 11,154
Basic Blue 99	C. I. No. 56,059
Basic Brown 4	C. I. No. 21,010
Basic Brown 16	C. I. No. 12,250
Basic Brown 17	C. I. No. 12,251
Basic Green 1	C. I. No. 42,040
Basic Red 2	
Basic Red 22	
Basic Red 76	C. I. No. 12,243
Basic Violet 1	C. I. No. 42,535
Basic Violet 3	C. I. No. 42,555
Basic Violet 10	C. I. No. 45,170
Basic Violet 14	C. I. No. 42,510
Basic Yellow 11	
Basic Yellow 57	C. I. No. 12,719

The following acidic (anionic) dyes may possibly find application:

Acid Black 1	C. I. No. 20,470
Acid Blue 9	C. I. No. 42,090
Acid Blue 74	C. I. No. 73,015
Acid Red 18	C. I. No. 16,255
Acid Red 27	C. I. No. 16,185
Acid Red 87	C. I. No. 45,380
Acid Red 92	C. I. No. 45,410
Acid Violet 43	C. I. No. 60,730
Acid Yellow 1	C. I. No. 10,315
Acid Yellow 23	C. I. No. 19,140
Acid Yellow 3	C. I. No. 47,005
D&C Brown No. 1	C. I. No. 20,170
D&C Green No. 5	C.I. No. 61,570
D&C Orange No. 4	C.I. No. 15,510

D&C Orange No. 10	C.I. No. 45,425:1
D&C Orange No. 11	C.I. No. 45,425
D&C Red No. 21	C.I. No. 45,380:2
D&C Red No. 27	C.I. No. 43,410:1
D&C Red No. 33	C.I. No. 17,200
D&C Yellow No. 7	C.I. No. 45,350:1
D&C Yellow No. 8	C.I. No. 45,350
FD&C Red No. 4	C.I. No. 14,700
FC&C Yellow No. 6	C.I. No. 15,985

The concentration of direct-acting dye in the compound according to the invention is variable and lies between approximately 0.01 to approximately 1.5, preferentially 0.05 to 1, particularly 0.1 to 0.5% by weight of preparation.

The hair coloring and toning means according to the invention preferably contains at least one synthetic or natural hair-conditioning polymer, preferentially in an amount from 0.1 to 2.5, particularly 0.25 to 1.5% by weight of preparation. Although basically all types of polymers can be used: non-ionic, ionic, amphoteric and cationic polymers, cationic polymers are preferred within the framework of the invention.

As such, in addition to the well-known quaternary cellulose derivatives of the "Polymer JR" type, the quaternary homo- and co-polymers of dimethylidiallyl ammonium chloride, obtainable commercially under the trade name "Merquat," quaternary vinylpyrrolidone copolymers, particularly with dialkylaminoalkyl(meth)acrylates, known under the name "Gafquat," copolymers of vinylpyrrolidone and vinylimidazoliniummethochloride, which are available under the trade name "Luviquat," polyamino-polyamide derivatives, for example, copolymers of adipic acid dimethylaminohydroxypropyldiethylenetriamine, which is sold under the name "Cartaretine F," as well as the by quaternary long-chain ammonium compounds of the ammonium structures described in US-PS 4 157 388 that are sold under the trade name "Mirapol A 15."

Reference is also made in this connection to the cationic-active polymers mentioned in DE-OSS 25 21 960, 28 11 010, 30 44 738 and 32 17 059 as well as the products described on pages 3 through 7 of EP-A 337 354. Mixtures of various cationic polymers may also be substituted.

Instead of the cationic polymers or in combination with them, non-ionic polymers can also be added. Suitable non-ionic polymers are primarily vinylpyrrolidone homo-and co-polymers, particularly polyvinylpyrrolidone itself, copolymers of vinylpyrrolidone and vinyl acetate or terpolymers of vinylpyrrolidone, such as are produced by the firm BASF under the trade name of "Luviskol."

Also (co-) polymers of the various acryl and methacryl esters, acrylamide and methacrylamide, for example, polyacrylamides with molecular weights above 100,000, dimethylhydantoin-formaldehyde resins etc. may be added. Naturally, mixtures of various non-ionic polymers may also be used.

Suitable anionic polymers within the framework of the invention are vinyl alkyl ethers, particularly methyl vinyl ether/malonic copolymers, which are produced through hydrolysis of the vinyl ester/malonic acid and hydride copolymers and sold under the trade name "Gantrez AN or ES." These polymers may also be partially estered, for example "Gantrez ES 225," the Ethel Aster of an Ethel vinyl ethers/malonic acid copolymer or the usual or isobutyl esters of these.

Further suitable anionic polymers are in particular vinyl acetate/crotonic acid or vinyl acetate/vinylneodecanoate/crotonic acid copolymer of the "Resyn" type; sodium acrylate/vinyl alcohol copolymers of the "Hydagen F" type, sodium polystyrolsulfonate, for example, "Flexan 130"; Ethelacrylate/acrylic acid/N-tert. Butylacrylamide copolymer of the "Ultrahold" type;

vinylpyrrolidone/vinyl acetate/itaconic acid copolymers, acrylic acid/acrylamide copolymers and sodium salts of days of the "Reten" type etc.

Basically all of the anionic polymers recommended as additives in haircare preparations can be used.

Among amphoteric polymers, which may be used either alternatively or in mixtures with others, particularly cationic polymers, one may especially mention copolymers of N-octylacrylamide, to a (meth)acrylic acid and tertiary butylaminoethylmethacrylate of the "amphomer" type, copolymers of methacryloethylbetaine and alkylmethacrylateine of the "Yukaformer" type, for example, the butylmethacrylate copolymer "Yukaformer AM75," copolymers of monomers containing carboxyl groups or sulfo groups such as (meth)acrylic acid and itaconic acid with basic monomers, particularly those containing amino groups such as mono- and di-alkylamino alkyl(meth)acrylamides, copolymers of n-octylamide, methylmethacrylate, hydroxypropylene methacrylate, N-tert.-butyl aminoethylmethacrylate and acrylic acid as well as the copolymers known from US-A 3,927,199.

The color conditioning means according to the invention may also contain the usual additives, the type and character of which depend upon the application form of the preparation. These may be surfactants, particularly anionic surfactants such as long-chain N-acrylaminocarbonic acids and their salts such as N-laurylsarcocinate and -glutamate, amphoteric surfactants such as betaine, for example, cocoamidopropylbetaine, as well as non-ionic and cationic surfactants, fats, fatty alcohols, emulsifiers, pH regulators, solvents and binders, solubilizers, preservatives, perfumes etc.

The color conditioning means according to the invention may be in the form of an emulsion, dispersion or solution and also may be prepared as an aerosol foam. These preparations and their manufacture are thoroughly known to specialists and need no further explanation.

Particularly preferable are aqueous or aqueous-alcoholic solutions, based, for example, on 80 to 95% water and 5 to 20% lower alcohol such as ethanol, n-propanol or isopropyl alcohol.

The following examples describe the composition of the preparation according to the invention and illustrate its superiority over the conventional products.

## All proportions by weight

## Examples

	No. 1 Light brown	No. 2 Mahogany	No. 3 Medium blond
Hydroxypropyl guar	1.00		
Guar hydroxypropyltrimonium chloride		1.00	
Hydroxypropyl guar hydroxypropyltrimonium chloride			2.00
Polyquaternium-7	0.80	0.80	0.80
Cocoamidopropylbetaine	1.00	1.00	1.00
Dimethicone copolyol	0.10	0.10	0.10
Ethanol	5.00	5.00	5.00
Perfume	0.20	0.20	0.20
Basic Blue 99	0.066		
Basic Red 76		0.030	
Basic Brown 16			
Basic Yellow 57			
Basic Brown 17	0.050	0.200	0.036
Disperse Black 9	0.004		0.077
Disperse Blue 3	0.015	0.040	0.019
HC Red No. 3	0.060	0.350	0.024
Water ad	100.00	100.00	100.74

The substitution for the hydroxypropyl guar and the quaternary products by the same quantity of a conventional hydroxymethylcellulose leads to products whose dye uptake, that is, color intensity, measured after a 30-minute application at 30°C, measures an average of 20 to 25% less than with the composition according to the invention.

## Claims

1. Means of dyeing and toning human hair, containing at least one direct-acting dye in an aqueous or aqueous-alcoholic base, characterized in that it contains from 0.1 to 7.5% by weight, based on the total mixture, of at least one hydroxy-C<sub>2</sub>-C<sub>4</sub>-alkyl guar gum or its quaternary salts.
2. Means according to Claim 1, characterized in that it contains from 0.25 to 2.5% by weight, based on the total mixture, of at least one hydroxalkyl guar gum or its quaternary salts.
3. Means according to Claim 1 or 2, characterized in that it contains hydroxypropyl guar gum or a quaternary salt thereof as the hydroxy alkyl guar gum.
4. Means according to one or more of Claims 1 through 3, characterized in that it contains at least one cationic dye as the direct-acting dye.
5. Means according to one more of Claims 1 through 4, characterized in that it exhibits a pH value between 4 and 9.
6. Means according to one or more of Claims 1 through 5, characterized in that it contains from 0.1 to 2.5% by weight, based on the total mixture, of at least one hair-conditioning polymerene.